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14. ABSTRACT

Polydimethylsiloxane-aromatic dianhydride copolymers (PS Oxy-PAA and PS-DAH-PAA) were blended through several techniques with organoclays Cloisite 30B, 10A and Naþ ranging from 1 to 5 wt.%. Thermal and flame-retardant analysis revealed an in-situ blending approach was optimal, which led to the generation of a nanocomposite, PS-Oxy-PAA/30B (5 wt.%), with comparable heat release capacity (170.5 J/g-K) and total heat release (12.0 kJ/g) as seen with some commercial polymers. Concomittant dispersion and FTIR analyses revealed that the enhanced thermal stability observed with PS-Oxy-PAA/30B (5 wt.%) is not dispersion related, since the organoclay was exfoliated in all composites formed. The driving force is the interaction between the carbonyl groups of the PS-Oxy-PAA and the hydroxyl groups of the organoclay, which is limited in all other cases. These results suggest judicious selection of organoclay and siloxane copolymers can faciliate the design of new environmentally safe, heat processible, nonhalogenated alternatives to traditional flame-retardant polymers.

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Polysiloxane-based Organoclay Nanocomposites as Flame Retardants

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Polydimethylsiloxane-aromatic dianhydride copolymers (PS-Oxy-PAA and PS-DAH-PAA) were blended through several techniques with organoclays Cloisite 30B, 10A and Na^+ ranging from 1 to 5 wt.%. Thermal and flame-retardant analysis revealed an in-situ blending approach was optimal, which led to the generation of a nanocomposite, PS-Oxy-PAA/30B (5 wt.%), with comparable heat release capacity (170.5 J/g-K) and total heat release (12.0 kJ/g) as seen with some commercial polymers. Concomittant dispersion and FTIR analyses revealed that the enhanced thermal stability observed with PS-Oxy-PAA/30B (5 wt.%) is not dispersion related, since the organoclay was exfoliated in all composites formed. The driving force is the interaction between the carbonyl groups of the PS-Oxy-PAA and the hydroxyl groups of the organoclay, which is limited in all other cases. These results suggest judicious selection of organoclay and siloxane copolymers can faciliate the design of new environmentally safe, heat processible, nonhalogenated alternatives to traditional flame-retardant polymers.

Keywords Flame retardants; Nanocomposites; Organoclays; Polysiloxanes

INTRODUCTION

Halogen-based flame-retardant (FR) polymers and additives have been a cost-effective solution for FR applications. However, there is now an increased global emphasis on discontinuing the use of halogenated compounds due to the release of toxic gases upon combustion that are harmful to both humans and the environment. Thus, there exists the need to develop human and environmentally safe, economical polymers with efficient FR properties[1].

Polysiloxanes (PS) are oily materials with varying viscosities. An amine-terminated silicone oil (A12-PDMS) has previously been converted into various processable organic-inorganic hybrid copolymers using organic monomers through an environmentally benign, solvent-less approach[2]. The major combustion product of these PS copolymers is white silica, which is a nontoxic material used in many household applications. Pyrolysis-gas chomatography/mass spectrometry studies revealed that, upon combustion, cyclic siloxanes are released, which are nontoxic gases.

Subsequent studies have demonstrated that PS copolyimides, synthesized enzymatically, and copolyamic acids, synthesized in the absence of enzyme, were thermally stable and exhibited enhanced FR properties relative to copolyesters and copolyamides[3–5]. The thermal studies suggested that the polyamic acid portion of the polymers was acting as a heat sink via an endothermic reaction involving ring closure and imide bond formation. More recently, a novel class of boron-containing siloxane copolymers were synthesized employing boron as an additive, more specifically phenylboronic acid, during co-synthesis of aromatic dianydrides with A12-PDMS[6]. The resulting terpolymers demonstrated substantial thermal stability, dependent on boron concentration, and flame retardancy equivalent to select commerically available polymers.

Researchers have synthesized polysiloxane/clay composites and demonstrated that they are thermally stable and degrade into benign cyclic oligomeric siloxanes and higher oligomeric siloxane residues[7,8]. In this article, we report on the incorporation of organoclays in PS copolymers for further improvement of thermal and FR properties. PS copolymers containing organoclays have not previously been explored for FR applications. It is well-known that when polymers are combined with small amounts of organically modified clays (organoclays), the resulting composite can exhibit improved thermal, mechanical and FR properties[9–12].

Layered silicate nanoclays, in particular, are widely employed for organic-inorganic nanocomposite formation since the nanoclays contain chemically stable siloxane surfaces coupled with high surface areas, high aspect ratios and high strengths[13,14]. The inherent physical characteristics make the layered silicate nanoclays efficient reinforcing agents for polymeric systems[15,16]. Two important characteristics of the nanoclays make them useful as an additive in polymeric nanocomposites[9]: (i) the rich intercalation

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chemistry used to facilitate exfoliation of silicate nanolayers into individual layers, leading to maximizing interfacial contacts between organic and inorganic phases and (ii) the ability to modify their surface chemistries through ion-exchange reactions with organic and inorganic cations. The simple, environmentally friendly synthesis of PS organoclay nanocomposites, with varying compositions of organoclays produced by several blending conditions, is described. Thermal and FR properties as well as insight into the nanoclay interaction with the PS copolymer matrix are discussed.

EXPERIMENTAL

Materials

Aminopropyl terminated polydimethylsiloxane (A12-PDMS; MW 900–1100) was acquired from Gelest Inc. 4, 4′-oxydiphthalicanhydride (Oxy) and 1,1,4,4-tetracarboxylicphenyldianhydride (DAH) were purchased from Sigma-Aldrich. Organoclays were received from Southern Clay Products under the trademark name Cloisite®, specifically Cloisite Na^+, Cloisite 10A and Cloisite 30B. All chemicals were used without further purification.

Synthesis

Hand Blending of PS-Oximid, PS-Oxy-PAA and PS-DAH-PAA with Organoclays

Synthesis of PS-Oximid, PS-Oxy-PAA and PS-DAH-PAA copolymers were previously reported[3,4]. The PS-organoclays were prepared by melt blending three different organoclays with the three PS copolymers. In a typical procedure, PS-Oximid, PS-Oxy-PAA or PS-DAH-PAA (2 g; synthesized with 20–30% DAH or Oxy with respect to PDMS) was heated until it melted. Each organoclay was added to the PS copolymers in various percentages (1, 3, and 5 wt.%) and mixed thoroughly with a small spatula until a homogeneous mixture was obtained. The samples were allowed to cool to room temperature and were then dried in a vacuum desiccator overnight.

Blending Study of PS-Oxy-PAA and PS-DAH-PAA Organoclay Nanocomposites

PS-Oxy-PAA and PS-DAH-PAA organoclay nanocomposites were produced by three different methods: (A) melt blending, (B) in-situ blending, and (C) in-situ synthesis.

Method (A): PS-Oxy-PAA and PS-DAH-PAA (0.5 g; synthesized with 10% Oxy or DAH with respect to PDMS) was stirred/heated in a vial on a hotplate at 120°C for 20 min. Organoclay (5 wt.% with respect to PDMS) was added and the mixture was stirred/heated for 10 minutes. The mixture was immediately poured into a small glass petri dish and cooled to room temperature. It was then dried in a vacuum oven at 50°C overnight.

Method (B): A12-Silox PDMS (2 g) was stirred/heated in a vial on a hotplate at 70°C for 15 min. The temperature was increased to 120°C, 10 wt.% (with respect to PDMS) of dianhydride (Oxy or DAH) was added, and the reaction was stirred/heated for 30 min. Organoclay (5 wt.% with respect to PDMS) was added and the mixture was stirred/heated for 10 min. The mixture was immediately poured into a small glass petri dish and cooled to room temperature. It was then dried in a vacuum oven at 50°C overnight.

Method (C): A12-Silox PDMS (2 g) was combined with 5 wt.% (with respect to PDMS) of organoclay in a scintillation vial and sonicated for 24 h at 40°C. After 24 h, 10 wt% (with respect to PDMS) of dianhydride (Oxy or DAH) was added and the mixture was stirred/heated at 120°C for 30 min. The mixture was immediately poured into a small glass petri dish and cooled to room temperature. It was then dried in a vacuum oven at 50°C overnight.

Instrumental Analysis

Thermal decomposition was studied (under air) using a TA Instrument 2050 thermo gravimetric analyzer (TGA) with heating from 25–1000°C in ceramic pans at 20°C/min. Degradation temperature (T_d) is reported at 20% weight loss. Thermal decomposition kinetics were determined through TGA at various heating rates (5, 10, 15, 20, 25°C/min) using the Kissinger method (modified Arrhenius equation)[17] to calculate the activation energies for the thermal degradation processes. Flammability was measured using a pyrolysis-combustion flow calorimeter (PCFC, Fire Testing Technology Ltd. (FTT), UK). PCFC is a standardized nonflaming combustion method, which separately reproduces the gas phase and condensed phase processes of flaming combustion and forces them to completion in a single quantitative test using milligram sized samples and oxygen consumption calorimetry.

The heat release rate was calculated using the oxygen consumption principle. The heat release capacity (HRC) was then obtained by dividing the maximum heat release rate by the sample weight and heating rate. Total heat of combustion of degradation volatilities was calculated by direct integration of the heat release rate with time. Three measurements were carried out for each sample and the average of all three is reported. In cases where multiple peaks are observed in PCFC curves, the sum of all the peak heat release rates was analyzed to obtain HRC values using FTT software.

Organoclay-polymer interactions were probed by recording infrared spectra with a Thermo Nicolet 4700 Fourier Transform Infrared – Attenuated Total Reflectance (FTIR-ATR) spectrophotometer. Morphologies of the organoclay nanocomposites were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) employing a JEOL

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JSM-1401F FE-SEM and a Philips EM400 TEM respectively. Powder X-ray diffraction (XRD) analyses were carried out using an inXitu BTX X-ray diffractometer.

RESULTS AND DISCUSSION

Synthesis

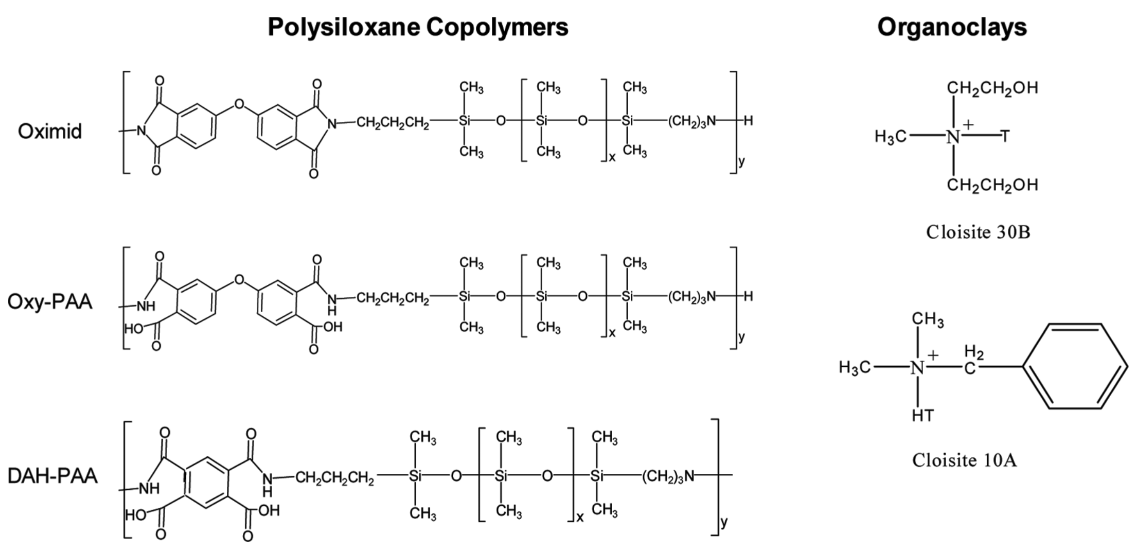
PS-Oximid, PS-Oxy-PAA and PS-DAH-PAA copolymers were synthesized without any solvents using simple one-step "green" methods previously reported[3,4]. The natural montmorillonite clays modified with a quaternary ammonium salt, Cloisite 30B (termed as 30b) and Cloisite 10A (termed as 10a), and an unmodified natural monmorillonite clay, Cloisite Na^+ (termed as Na^+), were melt blended respectively at varying concentrations with the PS-Oximid, PS-Oxy-PAA and PS-DAH-PAA copolymers (Scheme 1). This was accomplished by melting the PS copolymers and hand-blending in the organoclays with a small spatula until a homogeneous mixture was obtained.

Hemmati et al. have shown that clay concentration and mixing variables influence dispersion within the polymer matrix and resultant physical properties[18]. Olad and Hayasi have employed in-situ emulsion and bulk polymerization approaches to generate polystyrene/clay composites using similar monmorillonite clays employed here (Na^+, 30b, and Cloisite 15a) to reveal an influence upon d-spacing of silicate layers and improvement of thermal stability[19]. Moreover, an emulsifier-free emulsion polymerization technique has been employed for synthesis of polyacrylonitrile/clay nanocomposites[20]. With these considerations, as an alternative to hand blending, select polysiloxane organoclays were prepared by (A) melt blending, (B) in-situ blending and (C) in-situ synthesis. The methods were anticipated to provide further improvement to thermal and FR properties by facilitating more efficient interactions between the polymers and the different organoclays, as compared to hand-blending. Melt blending consisted of melting PS-Oxy-PAA or PS-DAH-PAA and blending in the organoclay with a stir bar. In-situ blending was achieved by synthesizing PS-Oxy-PAA and PS-DAH-PAA and immediately adding the organoclay and stirring with a stir bar prior to allowing the reaction to cool to room temperature. For in-situ synthesis, the organoclay was allowed to interact with the PS prior to initiating the synthesis. Analysis of the samples by thermal decomposition kinetics, thermal and FR properties, XRD, SEM, TEM and FTIR was carried out to assess the formulations.

FR Properties and Thermal Decomposition Kinetics

PS-Oximid, PS-Oxy-PAA and PS-DAH-PAA copolymers hand-blended with the three different organoclays (30b, 10a and Na^+) at 1, 3 and 5 wt.% were analyzed for thermal and heat release properties (supplementary information). To summarize, PS-Oximid organoclay nanocomposites exhibited T_d of 424–445°C, HRC of 241–376 J/g-K, and total heat release (total HR) of 16.4–18.3 kJ/g. PS-DAH-PAA organoclay nanocomposites displayed T_d of 462–493°C, HRC of 202–274 J/g-K, and total HR of 14.5–20.0 kJ/g. PS-Oxy-PAA organoclay nanocomposites presented T_d of 429–440°C, HRC of 159–210 J/g-K, and total HR of 12.9–18.2 kJ/g.

PS-Oximid nanocomposites did not improve thermal stability and provided minimal improvement in flame retardancy, relative to PS-Oximid, regardless of organoclay type and concentration employed. However, several other nanocomposites exhibited enhanced FR properties relative to PS-DAH-PAA and PS-Oxy-PAA. For instance, PS-Oxy-PAA/30b (5 wt.%) nanocomposite displayed a ~40% and ~20% enhancement in HRC and total HR respectively.



SCH. 1. Synthesis of PS organoclay nanocomposites by blending the PS copolymers with organoclays. T = Tallow and HT = Hydrogenated Tallow.

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Additionally, PS-DAH-PAA/Na^+ (3 wt.%) possessed a 20% enhancement in both HRC and total HR. Although there was a lack of definitive trends in the improvement of thermal properties in regards to the varying concentration or composition of the organoclay employed, a concentration of ≥3 wt.% organoclay appeared to typically generate more thermally stable composites. These results are comparable to organoclay blends with a polyvinyl chloride/acrylonitrile-butadiene-styrene matrix in which 5 wt.% organoclay showed optimal effects on mechanical stability[21].

Subsequent blending studies using methods A, B or C, as described previously, were carried out on PS-Oxy-PAA and PS-DAH-PAA polymers (10 wt.% Oxy or DAH relative to PDMS) incorporating 5 wt.% organoclay (30b, 10a or Na^+). Thermal degradation curves for each preparation method appeared similar (data not shown). Jafari et al. have shown that the organically-modified montmorillonite nanoclays melt-mixed blended with polpropylene/poly(trimethylene terephthalate) synergistically enhance thermal stability and reduce thermal decomposition rate[22]. Therefore, more in-depth thermal decomposition kinetic studies were performed to evaluate the thermal degradation rates of the methods A, B and C synthesized nanocomposites and to provide more detailed knowledge of the minimum thermal energy required to convert the nancomposites into thermal degradation products (i.e., surface char). TGA measurements at various heating rates (5, 10, 15, 20, 25°C/min), using the Kissinger method (modified Arrhenius equation)[17], were employed to calculate the activiation energy (E_a) for the thermal degradation processes. Degradation kinetic results for PS-Oxy-PAA/30b (5 wt.%) are summarized in Table 1.

As seen in Table 1, methods B and C had increased E_a compared to method A, which indicated that methods B and C provided more thermally stable composites. Method C, which possessed the highest E_a, represents the only blending approach resulting in composites with a slower thermal decomposition rate than that seen with the base copolymer. These thermal decomposition kinetics indicated that the in situ synthesis (method C) was the optimal approach to creating polysiloxane/organoclay composites. The PS-DAH-PAA composites formed through this blending study showed similar trends to those seen with PS-Oxy-PAA.

Thermal and heat release properties for in-situ synthesized PS-Oxy-PAA and PS-DAH-PAA organoclay nanocomposites containing 5 wt.% organoclay are shown in Table 2. PS-DAH-PAA organoclay nanocomposites exhibited T_d of 431–440°C, HRC of 211–255 J/g-K, and total HR of 17.7–18 kJ/g. In comparison, PS-Oxy-PAA organoclay nanocomposites displayed T_d of 433–440°C, HRC of 170–210 J/g-K, and total HR of 12.0–20.1 kJ/g. Although it is more dramatic in the PS-Oxy-PAA organoclay nanocomposites, the thermal decomposition temperatures have increased for all samples, relative to the copolymer. Several researchers have reported an increase in thermal stability of polymers with a small amount of organoclay due to barrier effects from the clays, which reduce the escape of volatiles[23–25]. The FR properties (HRC and total HR) also showed improvement relative to the copolymer for select nanocomposites. Guo et al. have shown analogous enhancement in flame-retardancy properties due to the incorporation of organoclays into a polymer/silicon system[26]. In comparison of method C to the hand blending approach, the majority of copolymer nanocomposites using the method C preparation resulted in an enhanced HRC. In contrast, the total HR of nanocomposites formed by hand blending were superior to that seen with method C formation, with the exception of PS-Oxy-PAA/30b.

When considering all thermal and FR properties synergistically, PS-Oxy-PAA/30b produced through in-situ synthesis represents the most thermally stable composite formed with HRC and total HR comparable or better than

TABLE 1
Thermal decomposition analysis of PS-Oxy-PAA/30b (5%) produced by methods A, B and C

Polymer	$T_d{}^a$ (°C)	$E_a{}^{a,b}$ (kJ/mol)
PS-Oxy-PAA	403	184.9 (3, 0.91)
Method A	430	135.5 (5, 0.92)
Method B	431	161.3 (3, 0.99)
Method C	437	220.8 (5, 0.99)

^{a}20% wt loss in air atmosphere;.
^{b}Values in parentheses are number of points and regression coefficient.

TABLE 2
T_d, HRC, and total HR of in-situ synthesized PS-Oxy-PAA and PS-DAH-PAA organoclay (5 wt.%) nanocomposites

Copolymer	Organoclay	$T_d{}^a$ (°C)	HRC^b (J/g-K)	Total HR (kJ/g)
PS-DAH-PAA	None	428	244.0	18.3
	30b	431	211.5	18.0
	10a	439	255.0	17.7
	Na^+	440	224.0	17.8
PS-Oxy-PAA	None	403	187.0	18.5
	30b	438	170.5	12.0
	10a	440	180.5	19.6
	Na^+	433	210.0	20.1

^{a}20% wt loss in air atmosphere;.
^{b}PCFC analysis of multiple peaks.

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commercially available FR polymers such as, polyether ether ketone (PEEK; HRC = 155 J/g-K; Total HR = 12.4 J/g-K) and Poly(*p*-phenyleneterephthalamide) (KEVLAR; HRC = 302 J/g-K; Total HR = 14.8 J/g-K)[27]. Cloisite 30b has previously been shown as an effective organoclay for incorporation into polymer matrices, as evidenced by the enhanced thermal effects in nanocomposites with poly (trimethylene terephthalate)[28].

Organoclay Dispersion and Interactions with the PS-Copolymers

In order to better understand how the organoclays were integrated within the polymers, and identify whether they were intercalated or exfoliated, powder XRD analysis was performed. Powder XRD patterns of the organoclays (30b, 10a, Na^+) and their nanocomposites (5 wt.% of organoclay) with PS-Oxy-PAA and PS-DAH-PAA copolymers are shown in Figures 1a–1c. The organoclays 30b, 10a and Na^+ exhibit XRD peaks at 4.84°, 4.61° and 7.94°, corresponding to the (001) planes with a d-spacing of 1.82 nm, 1.92 nm and 1.11 nm of the interlayer distances, respectively. As can be seen from Figure 1(a,b), the characteristic 4.84° and 4.61° diffraction peaks of the organoclays (30b and 10a) disappeared in the nanocomposite XRD patterns (even magnified by 2.5×). In addition, no diffraction peak from 2° to 4.84° was observed, indicating that no intercalation occurred. Similarly, the characteristic peak for the nonmodified clay (Na^+) was not seen in the XRD diffractograms of the nanocomposites (Fig. 1c). A small peak around 5.5° in the XRD patterns is attributed to the Kapton windows of the sample compartment. A broad peak around 11.98° is attributed to the amorphous nature of PDMS. It should be noted that the XRD patterns of the PS-Oxy-PAA and PS-DAH-PAA nanocomposites with all three organoclays are overlapped due to the same amount samples used in the XRD measurements. The absence of the characteristic XRD peaks of the organoclays suggests that the organoclays were exfoliated within all nanocomposites formed, regardless of copolymer or clay employed.

To further assess the dispersion characteristics of the nanocomposites, SEM and TEM examinations were carried out. SEM analysis indicated that the initial hand melt blendings yielded an inconsistent dispersion of the organoclays, with small clumps observed. A more uniform dispersion was achieved with samples produced by methods used in the blending study, in particular method C. Figure 2 shows SEM images of the in-situ synthesized PS-Oxy-PAA/30b (5 wt.%) nanocomposite. Although a few fragments of the organoclay are observed on the surface (Fig. 2a), the SEM cross-sectional view revealed a lack of organoclay clumping within the nanocomposite (Fig. 2b). All three methods (A, B and C) exhibited similar dispersion properties for both PS-Oxy-PAA and PS-DAH-PAA nanocomposites.

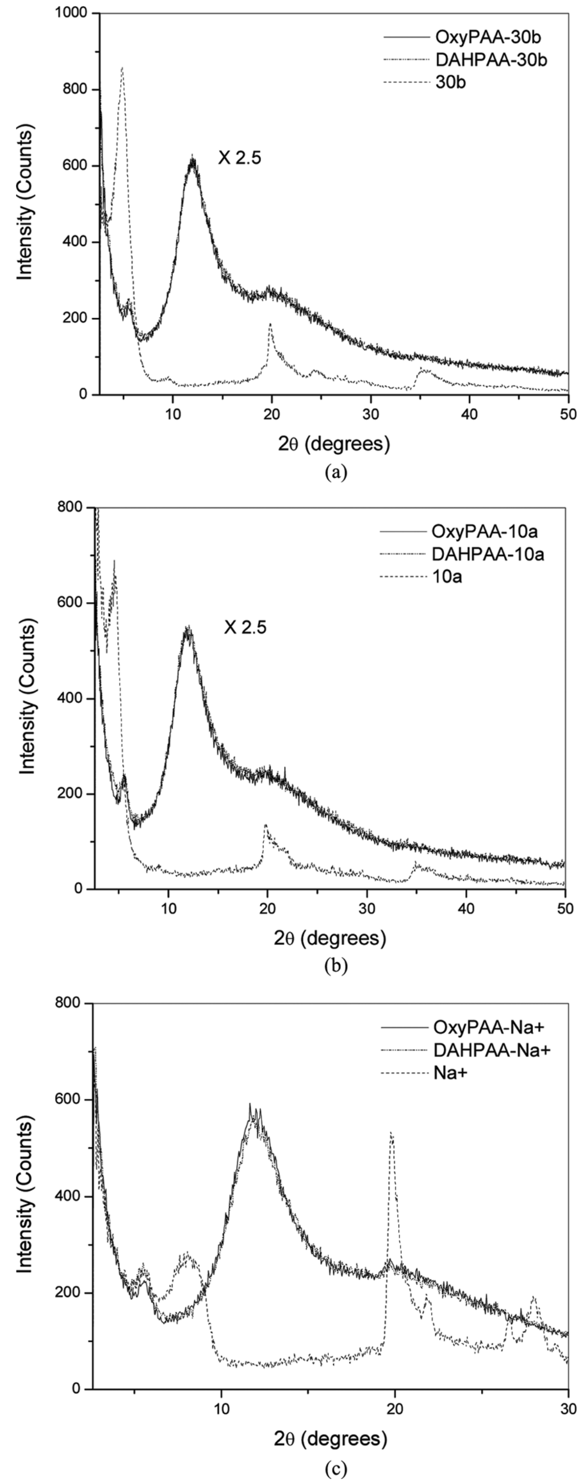

FIG. 1. XRD diffractograms of the PS-Oxy-PAA and PS-DAH-PAA nanocomposites with 5 wt.% of a) 30b, b) 10a and c) Na^+ and the corresponding organoclays.

A TEM image of the PS-Oxy-PAA/30b (5 wt.%) nancomposite is shown in Figure 3. The TEM micrograph suggests a homogeneous exfoliation of the nanosized clay

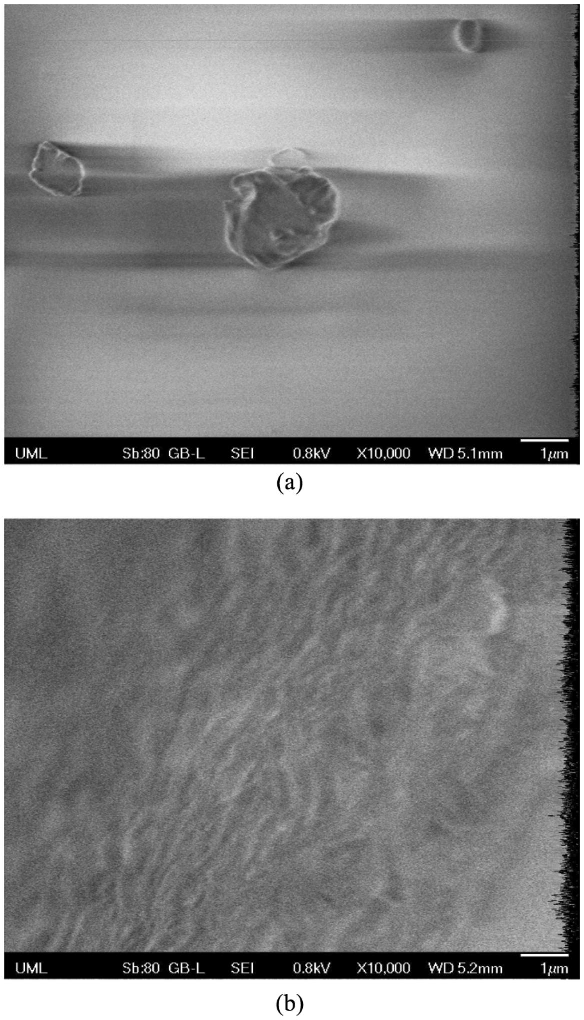

FIG. 2. SEM images of the in-situ synthesized PS-Oxy-PAA organoclay composite with 5 wt.% of 30b: (a) surface and (b) cross-sectional views.

layers (dark lines) within the polymer matix (light areas)[29]. A uniform distribution of the exfoliated organoclay was evident. Based on the compilation of XRD, SEM and TEM characterization, it is conjectured that the organoclays in all of the nanocomposites are exfoliated. Therefore, the differences in the thermal and FR properties of the nanocomposites observed in Table 2, particularily the enhanced properties seen with PS-Oxy-PAA/30b, appear due to other structural factors such as flexiblity and rigidity of the polymer monomers and the interactions of the organic components of the clays with the polymer monomers, as opposed to dependency on dispersive behavior.

To better define and understand the driving force behind the enhanced thermal and FR properties observed for PS-Oxy-PAA/30b (5 wt.%), FTIR-ATR analysis was conducted on the nanocomposites for elucidation of organoclay-polymer molecular interactions. PS-Oxy-PAA (Fig. 4a) and PS-DAH-

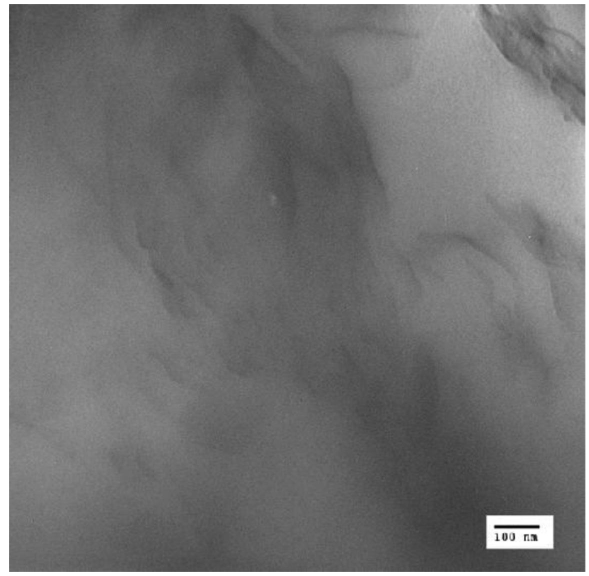

FIG. 3. TEM micrograph of PS-Oxy-PAA/30b (5 wt.%) organoglay nanocomposite at 14 kX. The organoclay layers (dark lines) are homogeneously exfoliated within the nanocomposite.

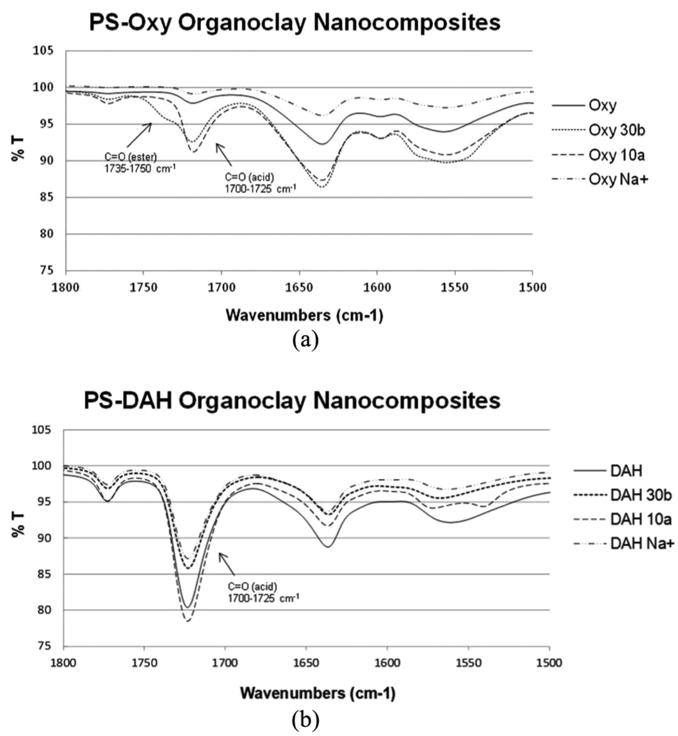

FIG. 4. FTIR-ATR of (a) PS-Oxy-PAA and (b) PS-DAH-PAA organoclay nanocomposites containing 5 wt.% organoclay. PS-Oxy-PAA/30b (5 wt.%) is the sole nanocomposite containing an ester, which may be due to the interaction between acid groups of PS-Oxy-PAA and the organic counter ion in 30b.

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PAA (Fig. 4b) polymers and their nanocomposites showed vibrational frequency at 1700–1725 cm^{-1}, which corresponds to the polyamic acid carbonyl (C=O). The PS-Oxy-PAA/30b (5 wt.%) results in a new band at 1735–1750 cm^{-1} with no other induced differences observed. The 1735–1750 cm^{-1} band corresponds to the vibrational frequency of the carbonyl group in an ester, which may be due to a strong interaction between the acid group of PS-Oxy-PAA and the hydroxyl groups of the organic counter ion in organoclay 30b. The 1735–1750 cm^{-1} band is not evident in other composites since the hydroxyl groups are not present in 10a or Na^+ organoclays.

Kato et al. have previously described interactions between polar groups with polypropylene and the oxygen groups of clay silicates [30]. The bond interactions have also been demonstrated between low density polyethylene and organoclay, which attributed to enhanced physical properties induced by composite formation[31]. The absence of interaction between the hydroxyl groups from 30b with PS-DAH-PAA could be due to the rigid nature of the DAH monomer. Interestingly, the rigidity of PS-DAH monomer contributed to enhanced HRC, compared to PS-Oxy monomer, when using boron as an additive[6]. In that case, rotation between PS-Oxy two phenyl rings may have contributed to a possible alternative thermal degradation mechanism, which was not observed with the PS-DAH single phenyl ring. Here, the observed thermal and FR stability of PS-Oxy-PAA/30b (5 wt.%) appears due to a specific molecular interaction of the clay with the copolymer, which is dependent on the chemical nature of the copolymer. The rigidity of PS-DAH may be detrimental to the molecular interaction with the organoclay while the flexibility of PS-Oxy facilitates the bonding. This suggests that dispersive behavior may be necessary for inclusion of clays into the polymer, but a bonding interaction between the clay and the copolymer backbone is the impetus behind enhanced thermal and FR stability.

CONCLUSIONS

In conclusion, PS organoclay nanocomposites were synthesized using simple environmentally friendly approaches, resulting in a novel class of potential FR materials. SEM indicated uniform dispersion of organoclays within the polymer matrices while TEM studies revealed a lack of agglomeration of the organoclays. XRD showed the disappearance of the organoclay peak and suggests that the organoclays are in an exfoliated state within the polymer matrix. FTIR analysis of the nanocomposites revealed a potential interaction between the carbonyl groups of the polymer and the hydroxyl groups of the 30b organoclay. The PS-Oxy-PAA (containing two phenyl rings with a bridging oxygen) organoclay nanocomposites consistently displayed more thermal protective properties with lower HRC than the PS-DAH-PAA (containing one phenyl ring) organoclay nanocomposites. The decrease of the HRC, with the addition of organoclays to the PS polymers, could be due to (i) interactions between the silicates of the clays and the siloxane copolymers; (ii) the interaction of the carboxylic acid groups with the hydroxyl groups of the organic counter ion of the clay; and (iii) the aromatic groups of the polymer with the benzene ring in the organic counter ion of the clay. This suggests that when designing new polymer organoclay nanocomposites, it will be helpful to consider the potential molecular interactions.

Lastly, these studies created a novel nanocomposite, PS-Oxy-PAA containing 5 wt.% organoclay 30b, which is a promising candidate for FR applications. The nanocomposite exhibits thermal stability and flame retardancy that is equivalent or surpassing current commerical FR polymers. The environmentally safe polymers and their resulting nanocomposites described herein are heat processable; therefore, studies are underway in our laboratory to develop new FR coatings for fabrics.

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